

CHARGE DISTRIBUTION ANALYSIS OF IRON OXIDE CATALYSTS*

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Abstract:

Catalytic reactions on solid contacts involve the exchange of charges across the solid/gas interfaces. Charge Distribution Analysis (CDA) is a new technique, capable of determining the generation of mobile charges in the bulk of materials and their appearance at the surface. By measuring the force acting on a sample in an electric field gradient, CDA derives unique information previously not available by any other technique. We have studied pressed pellets of two iron oxide catalysts supplied by the DOE Pittsburgh Energy Technology Center. α - Fe_2O_3 (hematite), heated in O_2 , behaves as a regular dielectric up to 450°C . The weakly negative surface charge indicates that electrons are the majority charge carriers. In Fe_3O_4 (magnetite), heated in N_2 , the surface is also weakly negative at ambient temperature, but evolves toward strongly positive values above 230°C . Upon cooling from 350°C this positive surface charge is firmly established, suggesting that defect electrons or holes have become the majority charge carriers. The trend toward positive surface charge continues up to 410°C when the composition of the magnetite sample starts to change. Between 275 – 410°C the magnetite is catalytically highly active toward dealkylation of 6-methyl-9-(1-methylethyl) dibenzo thiophene-4-ol. The fact that the catalytic activity toward dealkylation coincides with the appearance of a positive surface charge suggests that the active magnetite surface acts as an electron acceptor.

INTRODUCTION

Whenever chemical reactions occur, they involve the transfer of electrical charges between reacting partners. When one of the partners is a solid and the reaction occurs catalytically at its surface, the onset of reactivity will be marked by the appearance of charge carriers in the bulk of the catalyst and their diffusive transport toward the active surface.

In principle, the appearance of charge carriers should be amenable to electrical conductivity measurements. However, conventional conductivity techniques require electrodes that are in direct contact with the sample surface. Obviously, this can cause many problems. If the electrode-sample contacts are good, the surfaces are no longer free and unperturbed. In the case of high surface area samples good physical contacts are impossible to establish. It is therefore fair to say that conventional electrical conductivity techniques appear not to be well suited to study catalytic reactivity – unless a method can be developed which allows contact-free measurement of the electrical conductivity.

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CHARGE DISTRIBUTION ANALYSIS - A POWERFUL NEW TECHNIQUE

Charge Distribution Analysis (CDA) is a non-contacting technique that allows conductivity measurements of insulating and semiconducting materials under minimum perturbation conditions ^{1,2}. CDA is based on the dielectric polarization at the limit of 0 Hertz. When a dielectric is placed in an external electric field of field strength E_{ext} it becomes polarized. Its polarization P is:

$$P = \frac{\epsilon_0(\epsilon-1)}{4\pi} E_{ext} \quad (1)$$

where ϵ_0 is the permittivity of vacuum and ϵ the dielectric constant. P contains five contributions, $P_{el} + P_{ion} + P_{local} + P_{space} + P_{surface}$, of which the first two refer to the ideal dielectric. P_{el} reflects the electronic polarization of the electronic shells and P_{ion} the ionic polarization due to the field-induced atom displacement. The remaining three contributions arise from defects and impurities. P_{local} reflects local defects that change their intrinsic polarizability or dipolar defects that can rotate in the externally applied electric field. P_{space} arises from the space charge polarization due to mobile charges that can diffuse inside the sample. $P_{surface}$ is uniquely related to the surface charge.

When a dielectric is placed in a field gradient along the z direction, a force F_z^\pm acts on the sample towards higher field density. Using Maxwell's equations, F_z^\pm is given to first approximation by:

$$F_z^\pm = - \int \nabla (P \cdot E_{ext}) dV \quad (2)$$

where the volume integral includes the sample but not the sources of the field. In the case of an ideal dielectric (only P_{el} and P_{ion}) F_z^\pm is invariant to the direction of the field gradient: $F_z^\pm = F_z^+(E_{ext}) = F_z^-(E_{ext})$. In a real dielectric the contributions from P_{local} and P_{space} also remain invariant. However, the $P_{surface}$ term is variant to field gradient reversal. It causes an attraction to or repulsion from the region of higher field density, depending upon the sign of the surface charge. To separate ($P_{el} + P_{ion} + P_{local} + P_{space}$) from $P_{surface}$ we form the linear combinations:

$$F_\Sigma = \frac{1}{2} (F^- + F^+) = - \frac{\epsilon_0(\epsilon-1)}{4\pi} \int \nabla \cdot E_{ext}^2 dV \quad (3)$$

$$F_\Delta = \frac{1}{2} (F^- - F^+) = - \int \nabla (P_{surface} \cdot E_{ext}) dV. \quad (4)$$

To evaluate $P_{surface}$, we introduce $a_\pm U^2$ where a_\pm is a constant:

$$F^\pm = F_1^\pm + a_\pm U^2 \quad (5)$$

$a_\pm U^2$ describes the ideal dielectric and the F_1^\pm are constants. F_Σ and F_Δ are then given as:

$$F_\Sigma = \frac{1}{2} (F_1^- + F_1^+) + \frac{1}{2} (a_- + a_+) U^2 \quad (6)$$

$$F_\Delta = \frac{1}{2} (F_1^- - F_1^+) + \frac{1}{2} (a_- - a_+) U^2 \quad (7)$$

F_Σ characterizes the bulk polarization and is sensitive to the generation of mobile charges. F_Σ is proportional to the square of the applied voltage. F_Δ characterizes the surface, its charge density and the internal electric field. F_Δ is linearly proportional to the applied voltage and its sign identifies the sign of the charge carriers, for instance electrons (negative) or holes (positive) that may be present in the catalyst sample. F_Σ and F_Δ provide unique information about fundamental properties such as the on-set of chemical reactivity of a catalyst that is not available by any other known technique.

EXPERIMENTAL

A PERKIN-ELMER TGS-2 thermobalance, equipped with a cup-shaped Pt-wound furnace (10 mm i.d. x 20 mm), was modified by the introduction of a circular bias electrode and a cylindrical ground electrode to create an asymmetrical capacitor of axial symmetry. The samples were suspended via a fused silica fiber, well insulated from ground, and placed into the region of the steepest electric field gradient, approximately 0.1–0.5 mm above the bias electrode. They were heated in 25°C increments, using a heating rate of 20°C/min. During the time at constant temperature the bias voltages were applied sequentially for 10–20 sec in increments of +20 V, 0 V and –20 V. The forces were recorded as apparent weight changes in the sensitivity range 0.1–1 mg full scale.

The samples studied were coarse powders of α -Fe₂O₃ (hematite), labeled Catalyst #7, and Fe₃O₄ (magnetite), which were both prepared by Dr. Malvina Farcasiu of the DOE Pittsburgh Energy Technology Center. The average grain size of the magnetite was 5 μ m and its specific surface area was of the order of 7 m²/g. Both powders were pressed dry into 6 mm diameter pellets, about 1.5 mm thick. The hematite was dried in N₂ at 150°C, heated in O₂ to 410°C, cooled to 380°C and reheated to 560°C. The magnetite was dried in N₂ to 150°C, then heated to 350°C ("2nd heating"). It was then cooled to 150°C and reheated to 500°C in N₂ with intermittent cooling from 400°C to 300°C and 450°C to 350°C ("3rd heating").

RESULTS

F_Z of the hematite sample increased slightly and approximately linearly with temperature up to 500°C as shown in Fig. 1a. This suggests that up to 500°C, the sample behaved as a near-ideal insulator. Above 500°C, the F_Z increased significantly, indicating that mobile charge carriers are being generated. F_A was negative over the entire temperature range as shown in Fig. 1b, indicating that the surface charge of the hematite is dominated by electrons. A slight tendency towards positive F_A values was noted after the intermittent cooling from 410°C to 380°C which, however, was overtaken by an even stronger trend towards negative F_A values above 450°C. In conjunction with the pronounced increase in F_Z above 500°C this response clearly suggests that the mobile charge carriers generated in the hematite above 450°C are electrons.

The magnetite exhibited a distinctly different behavior. As shown in Fig. 2a, the F_Z values during the 2nd heating increased linearly with a lesser slope up to 230°C than above 230°C. This suggests the appearance of mobile charge carriers in the higher temperature range. During the 2nd heating, F_A was initially very slightly negative and showed a trend towards more negative values up to 230°C as evidenced by Fig. 2b. Above 230°C, however, the trend reversed towards positive F_A values.

After cooling to 150°C and subsequent reheating (3rd heating) F_Z increased linearly from 230°C onward up to about 450°C with the same slope as during the 2nd heating as shown in Fig. 3a. During intermittent cooling and reheating cycles the F_Z values were found to be successively higher, indicating that mobile charge had been generated during the heating cycles which did not disappear or recombine during cooling. Above 450°C, F_Z increased more rapidly, but at the same time, the magnetite sample started to lose weight, probably due to changes in composition in the unbuffered N₂

atmosphere. Experimentally this is seen in the fact that F_{Σ} is no longer proportional to the square of the applied bias voltage.

F_{Δ} remained positive during the 3rd heating as shown in Fig. 3b. Only at low bias voltage (20V) did F_{Δ} still show the same trend towards negative values up to 230°C, followed by an evolution toward positive values. At the higher bias voltages the trend was towards positive values. During intermittent cooling up to about 410°C the positive F_{Δ} values were further enhanced, indicating that the mobile charge carriers generated in the temperature interval 230–410°C have a positive sign. This in turn suggests that they are defect electrons or holes. The magnitude of F_{Δ} , about 10% of F_{Σ} , indicates that the charge carrier density at the magnetite surface is rather high. However, quantitative data can be obtained only from single crystals, not from a pressed powder sample¹. Above 410°C F_{Δ} showed signs of degradation. Experimentally this is seen in the fact that F_{Δ} was no longer linearly proportional to the applied bias voltage.

DISCUSSION

The magnetite under study is active toward the dealkylation of 6-methyl-9-(1-methylethyl) dibenzo thiophene-4-ol in the presence of a hydrogen donor. In spite of its large average grain size (5 μm diameter, 7 m^2/g specific surface area), its catalytic activity is very high as illustrated in Fig. 4. The F_{Δ} values shown (left ordinate) correspond to those measured during 2nd heating at 100V while the percentage dealkylation was achieved after 1 hour (right ordinate) using 25 mg catalyst and 25 mg 6-methyl-9-(1-methylethyl) dibenzo thiophene-4-ol. Trial runs performed by Dr. Farcasiu for 5 hrs at 150°C and 210°C did not produce an measurable dealkylation. Though we are still at an early stage of the investigation it appears that the catalytic activity of the magnetite may be directly related to the appearance of mobile charge carriers at its surface. The positive charge of the carriers identifies them as defect electrons or holes. Hence, the magnetite surface is expected to act as an electron acceptor.

Obviously, the holes are produced in the bulk of the magnetite crystals and diffuse to the surface where they become available for surface–gas reactions. To achieve the high turn–over number required for the observed degree of dealkylation, a large number of holes must flow from the bulk to the surface. By performing time–dependent CDA experiments it should also be possible in the future to measure the diffusive mobility of these active charges. Such measurements are of interest, if one tries to correlate the rate of a catalytic reaction with the density of charges at the solid surfaces.

On the basis of the data so far available, the CDA technique seems to be a promising tool to evaluate the activity of catalysts and to obtain valuable information about the nature of the charge carriers which participate in or are instrumental for catalytic reactions³.

REFERENCES

- (1) Freund, M. M.; Freund, F.; Batllo, F. *Phys. Rev. Lett.* **1989**, *63*, 2096-2099.
- (2) Freund, F.; Batllo, F. *US Patent No. 4,884,031* **1989**,
- (3) Freund, F.; Maiti, G. C.; Batllo, F.; Baerns, M. *J. Chim. Phys.* **1990**, *87*, 1467-1477.

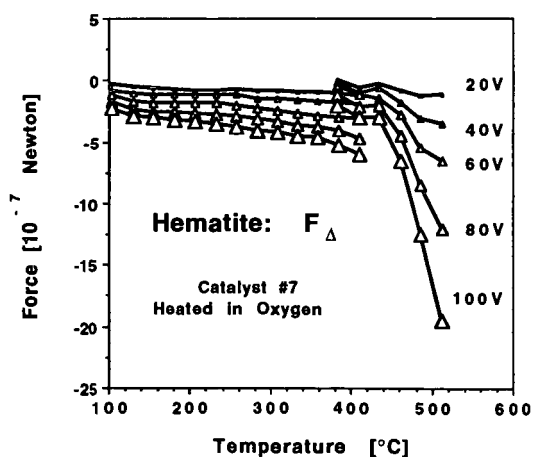
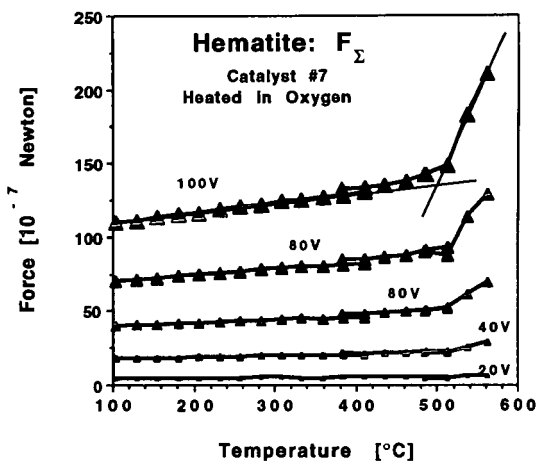


Fig. 1 a/b: F_{Σ} (top) and F_{Δ} (bottom) of hematite (Catalyst #7) heated in O_2 . The CDA response is typical for a near-ideal dielectric up to about 500°C . Throughout the temperature range studied, the dominant charge carriers are electrons.

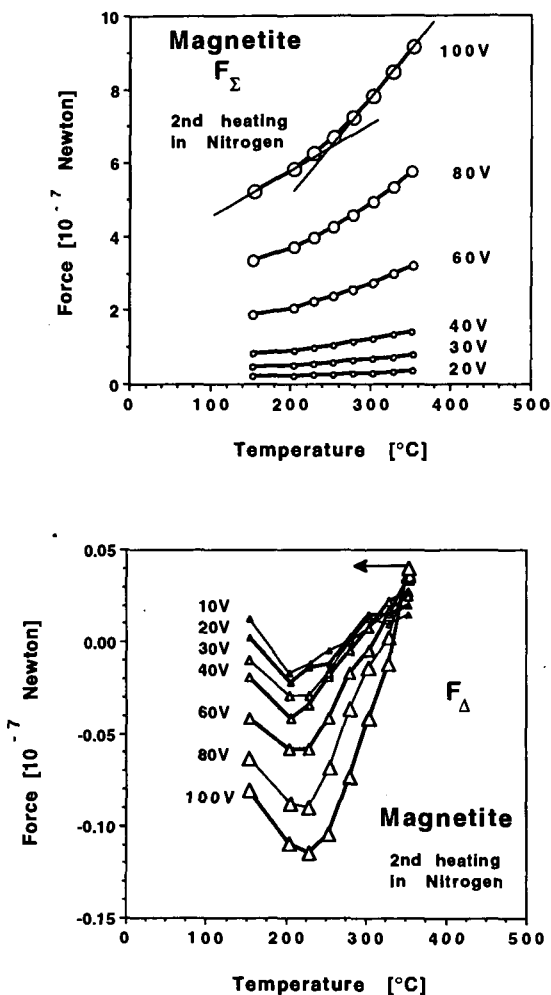


Fig. 2a/b: F_{Σ} (top) and F_{Δ} (bottom) of magnetite heated in N_2 . The CDA response suggests that, while electrons are the predominant charge carriers below 230°C , defect electrons or holes start to dominate at the higher temperatures.

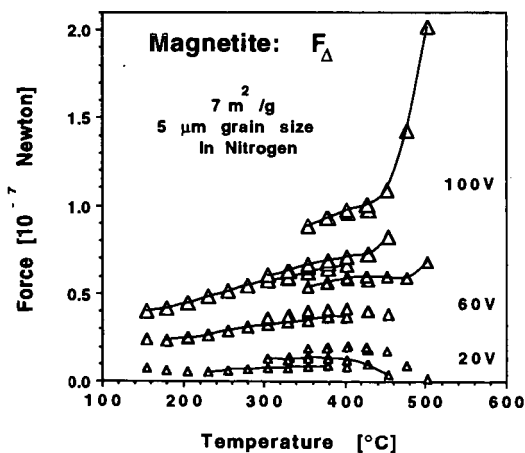
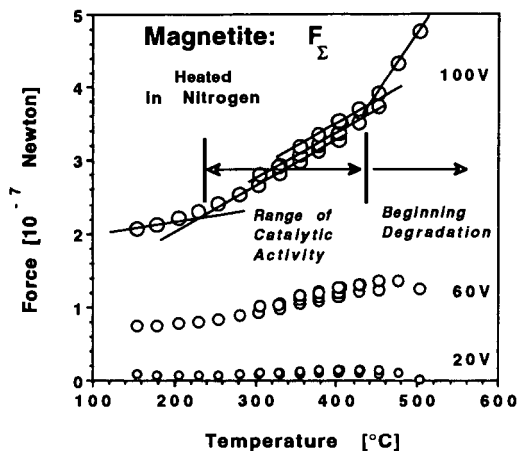


Fig. 3a/b: F_{Σ} (top) and F_{Δ} (bottom) of magnetite heated and intermittently cooled in N_2 . The CDA response of magnetite suggests that defect electrons or holes are the predominant charge carriers up to 450°C at which point decomposition sets in.

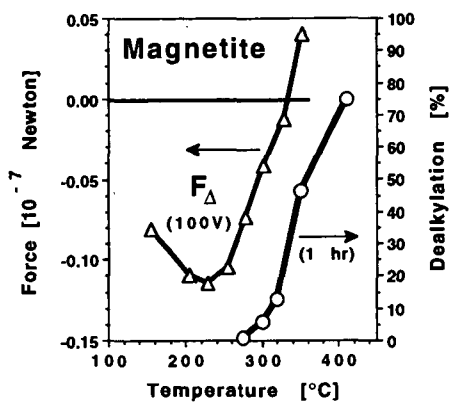


Fig. 4: Comparison between the surface charge of the magnetite sample in N_2 as measured by CDA, F_{Δ} (left scale), and the percentage of dealkylation of 6-methyl-9-(1-methylethyl) dibenzo thiophene-4-ol (right scale) after 1 hr. reaction time. At 150°C and 210°C no dealkylation occurred, even after 5 hrs. (Data courtesy of Dr. Malvina Farcasiu)